Synthesis and Molecular Weight Characterization of Rubber Seed Oil-Modified Alkyd Resins

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ABSTRACT: Alkyd resins of 40% (I), 50% (II), and 60% (III) oil length (OL) were prepared with rubber seed oil (RSO), phthalic anhydride (PA), and glycerol (GLY), employing the two-stage alcoholysis method. Changes in the physical characteristics of the reaction medium were monitored by determination of the acid value and the number-average molecular weight, $\overline{M}_n$, of in-process samples withdrawn at different stages of the reaction. The mode of variation of these properties denotes that the preparation of RSO alkyds is complex. Molecular weight averages and the molecular weight distribution (MWD) of the finished alkyds were determined by GPC, cryoscopy, and end-group analysis. Molecular weight averages and the MWD vary with differences in the formulation, with sample II exhibiting the narrowest size distribution. Values of $\overline{M}_n$ with the corresponding polydispersities in brackets are 3234 (1.91), 1379 (1.56), and 3304 (2.56) for samples I, II, and III respectively. $\overline{M}_n$ values obtained by cryoscopy are comparable to those obtained by gel permeation chromatography (GPC), while end-group analysis seems to grossly overestimate their molecular weights. Correlation of $\overline{M}_n$ and the MWD with the quality of the finished alkyds shows that the narrower the size distribution the better the quality of the alkyd. Properties such as the rate of drying and resistance of the alkyds are optimum at 50% OL. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 2431–2438, 2001

Key words: cryoscopy; end-group analysis; molecular weight averages; molecular weight distribution; rubber seed oil alkyds

INTRODUCTION

Alkyd resins have remained the foremost group of binders used in surface coatings due to their unique properties like color and gloss retention, film flexibility and durability, and compatibility with other resin systems. Their peculiar property

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of compatibility with binders such as acrylics and urethanes has facilitated their use in formulating environment-friendly coatings in recent times.[1–8] Therefore, the technology of alkyd production has continued to receive the attention of chemists.

Generally, alkyd resins are defined as products of condensation between polyol, usually having an average functionality equal to or greater than 3 and a polybasic acid, usually dibasic acid or its anhydride modified with monofunctional acid, most commonly C_{18} fatty acid or triglyceride.[9,10] Such a reaction involving the reactants of average functionality equal to or greater than 3 are prone to network formation arising from the possibility

of a 3-dimensional reaction. As characteristic for such synthetic polymers, they are polydispersed, comprising species of varying molecular sizes; hence, their properties are dependent upon the average molecular weight as well as on the molecular weight distribution (MWD) about this average.[11] For instance, it has been observed that the performance quality of alkyd resins as binders becomes optimum at a point during the synthesis when molecules of appreciable sizes are formed.[11,12] The rate of oxidation of alkyd films and their chemical and mechanical properties have also been found to be related to the average molecular weight of the alkyd resin.[13,14] Similarly, the stability of alkyds on storage and their solubility in conventional hydrocarbon solvents, for example, white spirit, commonly employed in modifying their viscosity, are both dependent on their average molecular weights.[15] Therefore, knowledge of their molecular weights and MWD is of utmost importance for both their characterization and as a means of evaluating their performance as binders in surface coatings.

However, in processing alkyds for optimum coating performance, it is required that the molecular weights are not too large; otherwise, the alkyd may convert into an intractable gel and become out of control or too low such that its coating performance is impaired.[15] Thus, alkyds of appreciable molecular sizes that would ensure trouble-free processing and exhibit stability on storage and perform well during service are desirable for the alkyd chemist.

Our previous efforts[16-18] indicated that rubber seed oil (RSO) is a potential candidate for substituting imported drying oils for use in the Nigerian surface coating industry. Thus, it was conceived that estimates of their relative molecular sizes vis-à-vis their coating performance is imperative for effective control of the reaction conditions leading to their production in order to guarantee a quality product. This constitutes the main objective of this study.

In the furtherance of our determination to develop RSO alkyds to an acceptable commercial standard, we carried out a study of their molecular weights and MWDs and correlated these with their performance as binders. Essentially, the study entailed monitoring of the acid value and average molecular weight of in-process samples as the reaction progressed in order to ascertain when the reaction medium attained structural complexity, the molecular weight characterization of the finished alkyds using GPC, cryoscopy,

Table I   Physicochemical Properties of RSO

Property	
Color	Dark
Specific gravity (30°C)	0.919
Free fatty acid (as oleic acid)	26.5
Acid value (mg KOH/g)	53.1
Saponification value (mg KOH/g)	206.2
Iodine value (g I_2/100 g)	135.4

and end-group analysis, and an evaluation of their quality. Our findings are herein reported.

EXPERIMENTAL

Materials

Rubber, *Hevea brasiliensis* Muell, Arg, seed oil (RSO) was obtained from M/s Kathivel & Bros. (Tamil Nadu, India). It consists of 18.9% saturation and 80.5% unsaturation with palmitic (10.2%) and stearic (8.7%) as the main saturated fatty acids and oleic (24.6%), linoleic (39.6%), and linolenic (16.3%) as the dominant unsaturated fatty acids. The physicochemical properties are shown in Table I.

Technical-grade phthalic anhydride (PA), glycerol (GLY), xylene, and lead(II) oxide obtained from the New India Chemical Enterprise (NICE) Pvt. Ltd. (Cochin, India) were used without further purification in the synthesis of the alkyds. A microanalytical reagent (MAR) camphor obtained from the Central Drug House (CDH) Pvt. Ltd. (India) was used in the cryoscopic studies while tetrahydrofuran (THF) from the British Drug House (BDH; Poole, England) was of HPLC grade and used in the GLC.

METHOD

Preparation of the Alkyds

Three grades of alkyd resins containing 40% (I), 50% (II), and 60% (III) oil content were prepared with PA, GLY, and RSO as per the formulation in Table II. The two-stage alcoholysis method as reported previously was employed in their synthesis.[17] In-process samples were withdrawn at time intervals for acid value and molecular weight determinations.

Table II   Formulation for the Alkyds

Ingredients	Alkyd Samples		
	I	II	III
RSO (moles)	0.456	0.575	0.702
PA (moles)	0.778	0.652	0.531
GLY (moles)	0.657	0.307	0.328
Alkyd constant, k	1.02	1.02	1.02

Gel Permeation Chromatography (GPC)

GPC was performed on a Hewlett–Packard 1081 B HPLC with a refractive index detector for eluate monitoring. It consists of three μ-Styragel HT3 columns of dimension 300 × 7.5 mm and porosity 100, 500, and 1000 Å (Waters Associates) arranged in series. The chromatograms and integrated data were recorded automatically with a Chromatopac C-R 3A processor (Shimadzu) using the Waters Associate programming version 3.0.

HPLC-grade THF was used as the mobile phase and the sample concentration was 2% w/v. Two hundred microliters of the solution was injected into the column at a temperature of 40°C. The flow rate was 1 mL/min and the run time was 18 min.

Propylene glycols of various molecular weights were used as internal standards. Figure 1 shows the calibration curve obtained by plotting log molecular weights versus retention times.

Cryoscopy

Number-average molecular weights, $\overline{M_n}$, of in-process samples as well as those of the finished alkyds were determined by the cryoscopic method employing the freezing-point depression of camphor.[19]

Properties and Performance Evaluation of the Finished Alkyds

The following standard test methods were used to evaluate the properties and performance characteristics of the finished alkyds: physicochemical properties such as the acid value, iodine value, nonvolatile matter and saponification value (ASTM D 2689-73), viscosity (ASTM D 1725-62), drying schedule (ASTM D 1640-69), and the resistance of dry films (ASTM D 1308-57).

Theory of End-group Analysis

The acid value of in-process samples withdrawn at time intervals were determined by titrating aliquots of the samples dissolved in a mixture of toluene and ethanol (1 : 1) with a 0.1M KOH solution to the phenolphthalein endpoint. The extent of the reaction, P_{av}, and the average degree of polymerization, $\overline{DP}$, with respect to the acid value, were calculated using the following expressions[9,13]:

$$P_{av} = (C_0 - C_t)/C_0 \qquad (1)$$

$$\overline{DP} = (1 - P_{av})^{-1} \qquad (2)$$

where C_0 is the initial acid value and C_t is the acid value after time, t, of the reaction.

The average molecular weight, $\overline{M_{av}}$, with respect to the acid value at different stages of the reaction were calculated thus[15]:

$$\overline{M_{av}} = W/(k - P_{av})e_A \qquad (3)$$

where W is the total weight of all the ingredients charged; k, the ratio of the total moles of all ingredients charged to total equivalents of the acid (m_0/e_A); and e_A, the total equivalent of the acid.

The number-average molecular weight, $\overline{M_n}$, of the finished alkyds were also estimated from end-group analysis using the equation[9,13]

$$\overline{M_n} = M_0(\overline{DP}) \qquad (4)$$

where $\overline{DP}$ is the average degree of polymerization computed from the acid value of the finished
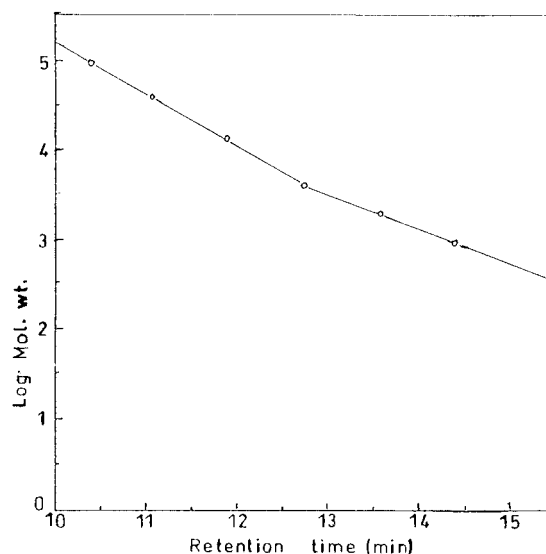

Figure 1   GPC calibration curve.

Table III   Acid Value (AV) of In-process Samples with the Corresponding Extent of Reaction (% P_{av})

Time (h)	I		II		III	
	AV (mg KOH/g)	P_{av} (%)	AV (mg KOH/g)	P_{av} (%)	AV (mg KOH/g)	P_{av} (%)
0	376.24	—	351.37	—	329.68	—
1	138.64	63.15	158.38	54.93	112.22	65.96
2	81.56	78.32	81.05	76.93	86.62	73.73
3	67.33	82.10	41.06	88.31	66.80	79.74
4	38.04	89.89	32.37	90.79	27.78	91.59
5	22.15	94.74	25.50	92.74	13.62	95.82
6	8.50	97.74	16.00	95.45	8.25	97.50
7	—	—	11.05	96.87	6.59	98.00

alkyds and M_o is the average molecular weight of the repeating unit of the alkyd and it is expressed as follows:

$$M_0 = \frac{RM_1 + PM_2 + GM_3}{R + P + G} \qquad (5)$$

In eq. (5), R, P, and G are, respectively, the number of moles of RSO, PA, and GLY used in the formulation and $M_1 = 272.4$, $M_2 = 132.0$, and $M_3 = 89.6$ are the approximate molecular weights of RSO, PA, and GLY, respectively, corrected for the possible loss of end groups.[13]

RESULTS AND DISCUSSION

Preparation of the Alkyds

The acid value of in-process samples determined at different stages of the reaction with the corresponding extents of the reaction are given in Table III. The initial acid value decreases as the oil length (OL) increases. It is also evident from the results in Table III that the reactions were more than 50% completed after about 1 h of the reaction. This observation can be rationalized on the basis of the different reactivities of α- and β-OH groups of glycerol. It was reported[20] that α-OH groups of glycerol react much faster than do their β counterparts. Thus, the initial rapid decrease in the acid value is thought to correspond to the time when α-OH groups reacted. A similar high rate of conversion during the early stages of the reaction between GLY and PA was reported.[21]

For polycondensation reactions, it was proposed that plots of $\overline{DP}$ against time should be linear throughout the reaction.[22] However, in Fig-ure 2, which shows plots of $\overline{DP}$ versus the reaction time for the alkyds investigated, two distinct portions are obvious: first, the initial linear portion, which is thought to correspond to a period when the α-hydroxyl groups of GLY reacted, and the second curved portion, which corresponds to when the β-hydroxyl groups reacted. This region of deviation from linearity in these plots is considered to mark changes in the physical characteristics of the reaction medium, most probably the period marking the beginning of the formation of relatively large molecular species and the crosslinking of the alkyd chains. The properties of the alkyds estimated at this region are given in Table IV. The extent of the reaction ranges from 76.9% for sample II to 82.1% for sample I. These values are in reasonable agreement with the values of 75 and 83.3% reported earlier.[21] The M_{av} obtained at this region ranged from 637 for sample II to 764 for sample III, while the M_{det} at this region is 265 for samples I and II and 367 for sample III. These molecular weight averages show that the reaction mixture is constituted of low molecular weight species. These values are also consistent with those reported for samples withdrawn at the verge of gelation during alkyd preparation.[12,23]

Plots of $\overline{M}_{det}$ for in-process samples versus the reaction time are shown in Figure 3. It can be seen in these plots that during the early stages (to 2 h) of the reaction there seems to be no substantial increase in the molecular sizes of the reaction mixture. Thereafter, an appreciable increase was observed, especially for sample II and after about 4 h for sample I. Furthermore, the shapes of these plots depict the complexity in the changes in the molecular sizes of the reaction mixture.
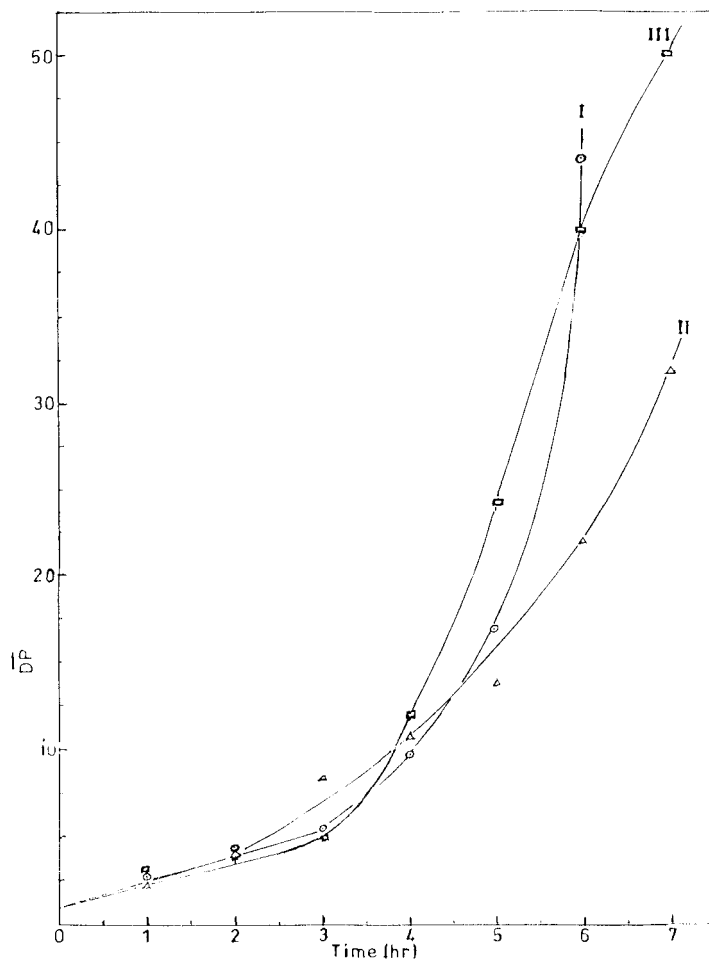
Figure 2   Plots of $\overline{DP}$ versus reaction time for the alkyds.

Molecular Weight Characterization

The GPC chromatograms of the alkyds shown in Figure 4 depict a broad size distribution. However, differences in the appearance of the chromatograms exist depending on the proportion of

Table IV   Properties of the Alkyds at the Region Where Plots of $\overline{DP}$ Versus Time Deviated from Linearity

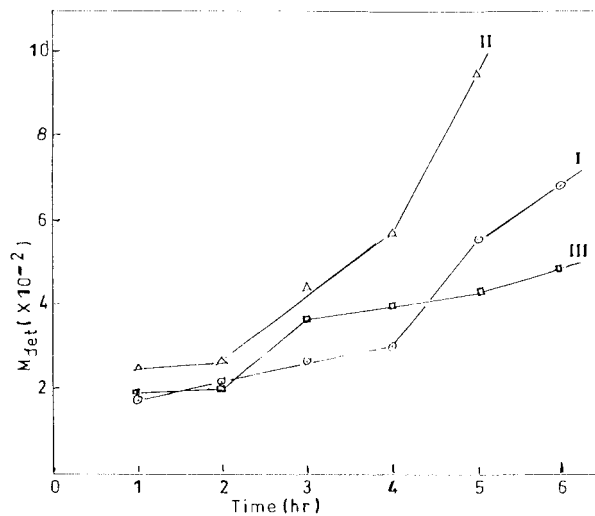| Alkyd Sample	Time (h)	Extent of Reaction (% P_{av})	$\overline{DP}$	Average Molecular Weight	
				$\overline{M}_{av}$	$\overline{M}_{det}$
I	3	82.10	5.59	749.27	265
II	2	76.93	4.34	636.85	265
III	3	79.74	4.94	764.40	367

Figure 3   Plots of $\overline{M}_{det}$ versus reaction time.
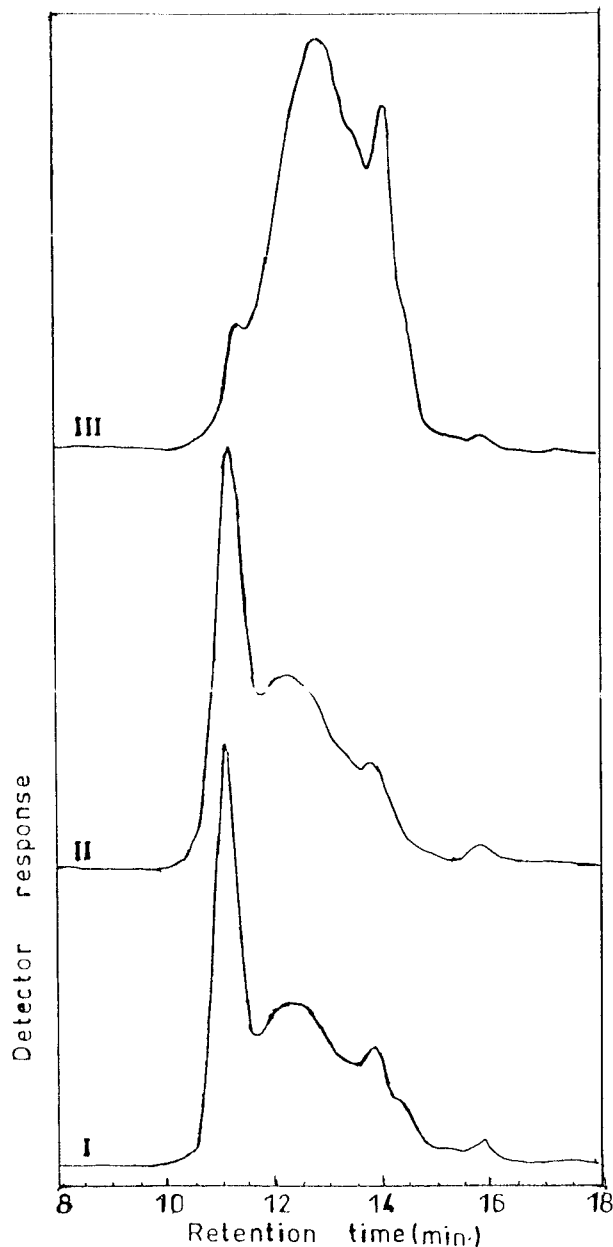
Figure 4 SEC chromatograms of the alkyds (Rubber Research Institute of Nigeria).

Table V   Molecular Weight Averages of RSO Alkyds Obtained by GPC

Alkyd Sample	Average Molecular Weight		MWD ($\overline{M_w}/\overline{M_n}$)
	$\overline{M_n}$	$\overline{M_w}$	
I	3234	6186	1.9
II	1379	2147	1.56
III	3304	8406	2.56

hence, a higher chance of the termination of chain growth.

The various molecular weight averages and the polydispersities are given in Table V. Both $\overline{M_n}$ and $\overline{M_w}$ vary in the order III > I > II. Values of $\overline{M_w}$ range from 2147 for sample II to 8406 for sample III, while $\overline{M_n}$ values with the polydispersity index in parentheses are 3234 (1.91), 1379 (1.56), and 3304 (2.54) for samples I, II, and III, respectively. These values are comparable with those of commercial alkyds.[25] The polydispersity indices clearly indicate that the size distribution is broad. However, sample II with the least value of 1.56 can be considered as being the most homogeneous.

The molecular weight averages of the finished alkyds obtained by cryoscopy and end-group analysis are presented in Table VI. These results show that there is good agreement between the $\overline{M_n}$ obtained by GPC and cryoscopy. However, end-group analysis seems to grossly overestimate the $\overline{M_n}$ of the alkyds. This discrepancy may be attributed to the assumptions made in the end-group analysis to the effect that the reactivity of the polymer chains is independent of its size, that the functional groups of the same kind are equally

Table VI   Molecular Weight Averages of RSO Alkyds Obtained by Cryoscopy ($\overline{M}_{\text{det}}$) and End-group Analysis ($\overline{M}_{\text{av}}$)

Alkyd Sample	Average Molecular Weight	
	$\overline{M}_{\text{det}}$	$\overline{M}_{\text{av}}$
I	2958 (−8.5)	6868 (+112)
II	1588 (+15.1)	6287 (+356)
III	3448 (+4)	13,301 (307)

Values in parentheses refer to the percent difference between these molecular weight averages and those obtained by GPC. (+) increase and (−) decrease over M_n value by GPC.

the reactants used. An abundance of high molecular weight fractions decreased as the OL increased. A similar trend was found for rape seed oil- and sunflower oil-modified alkyd resins.[24] This observation can be explained in terms of the function of monobasic fatty acids present in the oil. As a monofunctional component, they tend to terminate chain growth when they react. Thus, an increase in OL will increase the quantity of the fatty acids available for such reactions and,

Table VII   Properties of the Finished Alkyds

Property	Alkyd Sample		
	I	II	III
Color	Dark	Dark	Dark
Acid value (mg KOH/g)	8.27	9.85	4.70
Saponification value (mg KOH/g)	391.94	530.40	493.92
Iodine value (g I_2/100 g)	48.81	66.12	78.78
Viscosity (60% w/v; poise)	3.11	7.46	2.54
Specific gravity (at 30°C)	0.956	0.944	0.966
Nonvolatile matter (%)	69.21	74.03	64.76
Drying time			
Surface dry (min)	150–180	120	210
Dry through (h)	Overnight	Overnight	Overnight

reactive, and that intramolecular reactions are absent.[26–28] In practice, the occurrence of intramolecular condensation forming cyclic structures during polycondensation was reported.[29] Such intramolecular condensation will lead to a decrease in the level of acidity with increase in $\overline{DP}$ calculated therefrom without a corresponding increase in chain dimension.

Properties of the Finished Alkyds

Properties of the finished alkyds are given in Table VII. The dark color of the alkyds is due to the color of the RSO. All the alkyds were processed to an acid value below 10 mgKOH/g. Their higher saponification value than that of RSO is attributable to their being composed mainly of ester links. The iodine value of the alkyds decreases with a decrease in OL. The viscosity of the alkyds solution (60% w/v) ranges from 2.54 poise for sample III to 7.46 poise for sample II. This variation in the viscosity of the alkyds is consistent with the variation in the nonvolatile matter. Sample II exhibited the fastest drying rate.

Table VIII contains the results on the resistance of the alkyds. Generally, their resistance to water can be described as fair while their resistance to alkali is rather low except for sample II, which can also be regarded as fair. This may be explained on the basis of their consisting mainly of ester linkages which are susceptible to hydrolysis by water and alkali. This defect was found to be offset by modification with phenolic resins. However, RSO alkyds can be said to exhibit excellent resistance to acid and salt.

Correlation of the performance properties of the alkyds with their number-average molecular weights and MWD shows that the more polydispersed they are the less is their performance as binders. Thus, sample II, which has the narrowest molecular weight distribution, exhibited the best properties such as the fastest drying rate and resistance followed by sample I and then sample III.

CONCLUSIONS

In summary, it can be inferred from these results that reactions leading to the formation of RSO

Table VIII   Resistance of the Alkyd Films

Alkyd Sample	Resistance (After 16 h of Immersion)			
	Distilled Water	Alkali (N/10 KOH)	Acid (N/10 H_2SO_4)	Salt (5% w/v NaCl)
I	Little blister	Film removed	No effect	No effect
II	Film softened	Slight shrinkage	No effect	No effect
III	Film softened	Film removed	No effect	No effect

alkyds are complex. The MWD of RSO alkyds is a significant criterion that determines their performance as binders. The application properties of the alkyds are optimum at 50% oil modification. It could be a choice binder where moderate resistance is required or it could be enhanced by modification with phenolic resins.

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